Evidence of the superconducting energy gap in the optical spectra of α_t-(BEDT-TTF)$_2$I$_3$

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Abstract. – The far-infrared in-plane reflectivity of the organic superconductor α_t-(BEDT-TTF)$_2$I$_3$ is measured down to frequencies of 10 cm^{-1}; the optical conductivity is obtained by a Kramers-Kronig procedure. In the superconducting state an energy gap opens at 25 cm^{-1} which corresponds to $2\Delta/k_BT_c = 4.4$ in agreement with moderate coupling. Even well below $T_c = 8$ K a considerable absorption remains for $\hbar\omega < 2\Delta$. We discuss different posibilities to explain this behaviour.

Introduction. – Although organic superconductors have been under intensive investigations for two decades, the mechanism of superconductivity and the symmetry of the order parameter are still controversial [1]. Surprisingly, one of the key-experiments for superconductivity – the optical determination of the superconducting energy gap 2Δ – has not been successfully performed yet [2]. Soon after the discovery of superconducting BEDT-TTF salts with a transition temperature above 10 K, J. Eldridge and coworkers found no indications of a gap-related structure in the far-infrared absorption spectra above 10 cm^{-1} by using a sophisticated bolometric technique [3]. Their results could be understood if the organic materials were in the clean limit, i.e., $2\Delta > \hbar/\tau$ or $\ell > \xi$, with τ the scattering time, ℓ the mean free path, ξ the coherence length. This would mean that there is no noticeable spectral weight change in the range of the gap frequency. Alternatively the energy gap could be very small compared to the BCS prediction ($2\Delta/hc \approx 25$ cm^{-1} with a typical transition temperature of BEDT-TTF salts of 10 K) or even missing, either because the order parameter is very anisotropic but still s-wave like or the pairing symmetry is not s-wave.

Tunneling spectroscopy performed on various BEDT-TTF salts (mainly the κ-phase) gives no conclusive answer. Early reports claim a large energy gap of $2\Delta/k_BT_c = 9$ and a temperature dependence in full agreement with BCS predictions [4]. Other results [5–7] vary between samples but concurrently there seems to be some structure around $2\Delta/k_BT_c = 3.7$ and 7.4 which may indicate an anisotropic energy gap. Futher investigations still show a inconsistent picture [8] as far as the size and the temperature dependence of the gap are concerned. A

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recent STM study gives evidence of an anisotropic gap with d-wave symmetry and leads to values of $2\Delta/k_BT_c = 6.7$ within the highly conducting planes and to a somewhat larger ratio perpendicular to them [9]; no zero-bias conductance peak is observed. Various indirect methods to determine the superconducting energy gap [10] yield values in good agreement with the BCS predictions. However, a considerable number of experimental results point to gap nodes and are interpreted as indications for unconventional superconductivity [11]; for recent reviews see [1, 12]. Since the symmetry of the order parameter and the mechanism of superconductivity in the two-dimensional organic materials are highly controversial, we reconsidered the most direct method to investigate the superconducting energy gap by performing optical reflection experiments.

Experimental Results. – For our investigations we have chosen the α_t-(BEDT-TTF)$_2$I$_3$ compound because extremely large crystals of more than 5×3 mm^2 are available which have a high transition temperature of $T_c = 8$ K. Single crystals of α-(BEDT-TTF)$_2$I$_3$ were grown by standard electrochemical method and subsequently transformed to the superconducting α_t-phase by termpering at 70°C over a period of several hours [13]. Susceptibility measurements by a SQUID magnetometer indicate that the superconducting transition has an onset of 8 K but extends below 2 K because grain boundaries remain and internal stress is not fully released. In agreement with previous experiments the crystals are not completely transformed into the α_t-phase; we determine the superconducting volume fraction to be approximately 15%. From the BCS relation $2\Delta = 3.53k_BT_c$ we expected the gap around 20 cm^{-1}, i.e., at the lower end of the far-infrared spectral range. Thus we have utilized a coherent source spectrometer equipped with backward wave oscillators operating in the range from 2 to 45 cm^{-1} to study the reflectivity within the highly conducting plane. A home-made cryostat allowed to go to tempertures as low as 2 K. In order to increase the sensitivity for the comparably small changes of the reflection R upon the superconducting transition, we measured the ratio of $R(T < T_c)$ to $R(T > T_c)$ without moving the sample. The absolute value of $R(\omega)$ at a certain temperature T was then obtained by replacing the sample to a aluminum mirror of known reflectivity. The data were completed by standard reflection measurements using a Fourier-transform infrared spectrometer (inset of Fig. 1a). The low-frequency results at temperatures well above ($T = 15.0$ K) and below ($T = 3.6$ K) the superconducting transition are plotted in Fig. 1. After extrapolating to $\omega = 0$ with a Hagen-Rubens behaviour and to higher frequencies utilizing published data [14], we performed a Kramers-Kronig analysis to obtain the optical conductivity at different temperatures (Fig. 1b). Although small, the changes in the reflectivity and in the real part of the conductivity $\sigma_1(\omega)$ are reliably detected in our measurements: in the superconducting state the reflectivity increases and the conductivity decreases below approximately 40 cm^{-1}. Similar observations have been made on several crystals. The effects are better seen in Fig. 2 where the ratios are plotted: upon entering the superconducting state a significant increase in reflectivity is observed below 30 cm^{-1} with some undershot up to approximately 60 cm^{-1}. The transition to the superconducting state is also unambiguously seen in frequency dependent penetration depth of the electromagnetic radiation (inset in Fig. 1b) calculated by the general formula $\delta = c/(\omega k)$ where k is the extinction coefficient [15]. In a BCS superconductor $\delta(\omega)$ behaves Drude-like ($\delta \propto \omega^{-0.5}$) above the gap frequency, but decreases considerably and gets dispersionless for smaller frequencies [16, 17]. In our case only a slight decreasing and flattening of $\delta(\omega)$ is seen in the superconducting state, connected with the additional absorption processes which will be discussed below.

Analysis and Discussion. – For our further anaylsis we substracted the phonon contributions and mid-infrared bands from the conductivity spectra by fitting them with Lorentzians since only the free electrons are affected by the superconducting transition. In Fig. 2b the

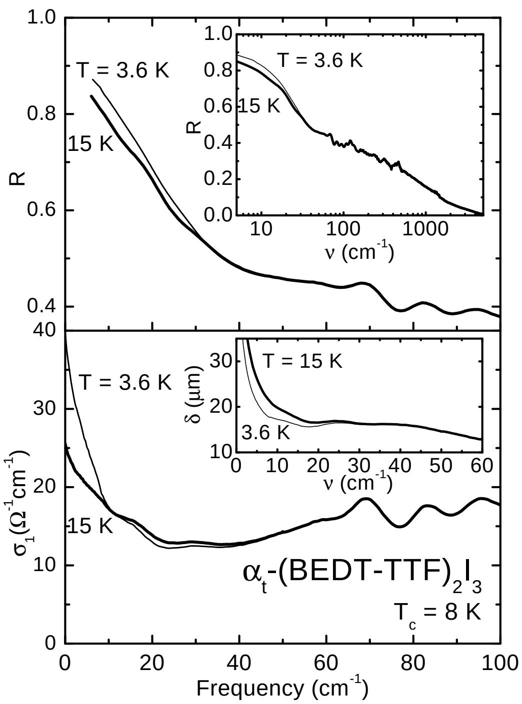

Fig. 1

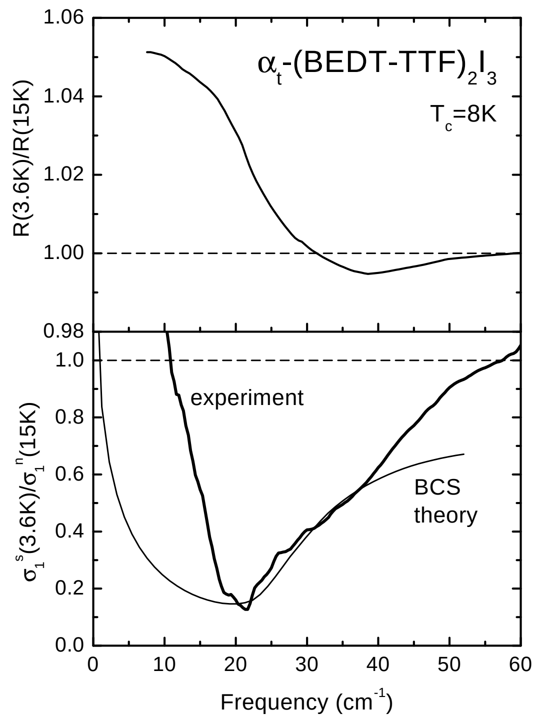

Fig. 2

Fig. 1 – (a) Frequency dependent reflectivity of α_t-(BEDT-TTF)$_2$I$_3$ at temperatures above and below the superconducting transition ($T_c = 8$ K). The inset shows the reflectivity at $T = 15$ K over a wide spectral range. The inset shows the reflectivity over a wide frequency range. (b) Corresponding conductivity spectra $\sigma(\omega)$ at $T = 15.0$ K and $T = 3.6$ K. The generalized penetration depth δ is plotted in the inset as a function of frequency (see text).

Fig. 2 – (a) Ratio of the reflectivity spectra of α_t-(BEDT-TTF)$_2$I$_3$ below and above the superconducting transition: $R(\omega, 3.6\text{ K})/R(\omega, 15\text{ K})$. (b) Frequency dependent conductivity $\sigma_1^s(\omega, T = 3.6\text{ K})$ in the superconducting state normalized to the normal state conductivity $\sigma_1^n(\omega, T = 15\text{ K})$ (see text).

ratio of the superconducting state and the normal state conductivity is plotted: $\sigma_1^s(\omega, T = 3.6\text{ K})/\sigma_1^n(\omega, T = 15\text{ K})$ taken the effective superconduting fraction into account [18]. We clearly see a dip in the conductivity spectrum as predicted by the BCS theory [15,16]. In a first approximation the minimum corresponds to the superconducting energy gap. Thus for α_t-(BEDT-TTF)$_2$I$_3$ we evaluate $2\Delta/hc = (25 \pm 3)$ cm^{-1} or $2\Delta/k_BT_c = 4.4 \pm 0.5$ in good agreement with what is expected for a medium to strong coupling BCS superconductor. We cannot make any profound statement on the temperature dependence of the gap frequency.

From the BCS weak-coupling model of an s-wave order parameter, at $T = 0$ there should be no absorption for energies below 2Δ because the photon energy is not sufficient to break the Cooper pairs, implying that $\sigma_1^s = 0$. With increasing temperature the $\omega = 0$ peak broadens and the gap gradually fills in due to thermal excitations of single-particles; only above $T/T_c \approx 0.5$ the gap starts to decrease noticeably according to the mean-field behaviour [15,16].

Most remarkably our results show a very broad $\omega = 0$ absorption peak which essentially extends all the way to the gap frequency. We thus conclude that there remains some additional absorption channel even at temperatures considerably below T_c connected with a low superconducting plasma frequency and large London penetration depth. We discuss three possibilities:
(i) The absorption in the superconducting phase might be due to intrinsic states in the energy gap. Similar observations are reported for the high-temperature superconductors where nodes in the gap are expected due to d-wave symmetry of the order parameter [17]. Calculations of the conductivity spectra using models with an anisotropic energy gap very much depend on the actual $\mathbf{k}$-dependence of the gap and whether there are nodes present or not [19]. In any case, at low temperature the absorption gradually increases starting from $\omega = 0$ to a maximum gap frequency $\Delta_{\max}/\hbar$. Qualitatively simlar behaviour is observed for an anisotropic gap or some $s + d$ symmetry which results in a vanishing absorption below some minimum energy gap $\Delta_{\min}$. Hence, these explainations are clearly in contrast to our observations.
(ii) If large parts of the sample are still in the normal state, we expect a background conductivity up to the frequency of the scattering rate. From Fig. 1b we see that the normal state conductivity contains a rather broad Drude component of $1/(2\pi c\tau_1) \approx 200$ cm^{-1} width and in addition a narrower Drude mode with $1/(2\pi c\tau_2) \approx 10$ cm^{-1}. Similar observations have been made in most organic conductors [2]. The observed behaviour could be explained using a two-band model where only one band contributes to superconductivity. The actual bandstructure of α_t-(BEDT-TTF)$_2$I$_3$ is not know. While in the original α-phase in general two bands cross the Fermi energy, the structure of the β-phase which is assumed to be close to that of the α_t-compound has only one cylindrical Fermi surface [20]. For some superconducting heavy fermions it was suggested that only the electrons at one part of the Fermi surface become superconducting [21], nevertheless such a scenario seems very unlikely in the present case.
(iii) The additional below-gap absorption in the superconducting state might be due to strong influence of the low frequency phonons and could be treated in the framework of the Eliashberg theory. Such treatment allows, in addition to a better fit of the detected low-energy absorption, also to describe the high-frequency wing of the gap feature where the changes upon entering the superconducting state are confined to about twice the gap energy, in contrast to the usual BCS behaviour. Since the actual low-frequency phonon spectrum is not known for this compound we restrained ourselves from performing a detailed fit. We want to note, however, that resonant Raman experiments on α_t-(BEDT-TTF)$_2$I$_3$ show a vanishing of low-energy phonon bands at 32 and 42 cm^{-1} below T_c [22].
Thus some alternative mechanism for the absorption seems to be relevant.

The changes in the conductivity spectra in the superconducting state are rather small (as compared to conventional or high-T_c superconductors), leading to a correspondingly small spectral weight of the superconducting condensate (δ-peak). This spectral weight can be estimated from the missing area in the conductivity spectrum which we calculate as the difference between the area under the $\sigma_1^n(T = 15$ K) and the $\sigma_1^s(T = 3.6$ K) spectra (starting with the frequency 10 cm^{-1}). Thus we get the plasma frequency of the condensate $\omega_p^s \geq 25$ cm^{-1}, and also estimate correspondingly the London penetration depth as $\lambda_L = c/\omega_p^s \leq 6$ μm. Magnetization measurements gave $\lambda_L \approx 430$ nm [23] for the in-plane penetration depth. Our values of ω_p^s and λ_L contain some uncertainty since we had to make assumptions on the reflectivity and, correspondingly, the conductivity below 10 cm^{-1}. Nevertheless, our results on λ_L are in good agreement with reports of a few μm for other BEDT-TTF salts [1, 2].

It remains to be seen whether these findings can be generalized to other organic superconductors. In particular the κ-phase of the BEDT-TTF salts would be of high interest because for these compounds the wealth of informations has been accumulated over the years. The corresponding optical experiments are in progress.

Conclusion. – We performed in-plane optical reflection experiments on the organic superconductor α_t-(BEDT-TTF)$_2$I$_3$ and determined an energy gap of 25 cm^{-1} which opens in the superconducting phase below $T_c = 8$ K and corresponds to $2\Delta/k_BT_c = 4.4$ (moderate coupling). The strong low-frequency absorption which remains in the superconducting state cannot be fully explained yet. The London penetration depth λ_L is estimated as 6 μm.

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